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THE GROWTH OF DEACTIVATED LAYERS  
ON CsI(Na) SCINTILLATING CRYSTALS

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THE GROWTH OF DEACTIVATED LAYERS  
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ABSTRACT

It has been previously reported that a layer which exhibits the scintillation characteristics of unactivated cesium iodide exists on the surfaces of some sodium activated cesium iodide [CsI(Na)] crystals. An effective and sensitive measurement of the depth of this deactivated or dead layer can be obtained from the relative attenuation of the 22.162 KeV and 87.9 KeV X-rays emitted by  $\text{Cd}^{109}$ . The  $\alpha$ -particles emitted by  $\text{Am}^{241}$  are also useful in measuring dead layers  $< 25 \mu$ . The properties and temporal development of dead layers are discussed here in detail.

The rate of growth of a dead layer is closely related to the ambient humidity and the damage to the crystal is irreversible by any known process. The dead layer can be minimized by polishing all crystal surfaces and by keeping the crystal in a vacuum or a dry atmosphere. Since a dead layer seriously inhibits the response of a crystal to X-rays of energies below  $\approx 20 \text{ keV}$ , CsI(Na) detectors should not be used at these energies unless extreme precautions are taken to ensure that no dead layer forms.

## I. INTRODUCTION

Sodium activated cesium-iodide [CsI(Na)] is used in many cosmic high-energy X-ray detectors both as the primary scintillation element and as the active anticoincidence shield.[1,2] Although it produces about 20% less light<sup>†</sup> output than thallium activated sodium-iodide [NaI(Tl)], CsI(Na) is preferred because it is mechanically and thermally more rugged and is also much less hygroscopic. It is consequently easier to machine and handle and need not be subject to as stringent precautionary measures as must NaI(Tl).

It has been previously reported [3] that after a few days exposure to the laboratory atmosphere the response of CsI(Na) to the 4.8 MeV  $\alpha$ -particle emitted by  $\text{Am}^{241}$  resembles that of unactivated cesium-iodide (CsI). The pulses were  $1\frac{1}{2}$  orders of magnitude smaller than those from fresh surfaces of CsI(Na) and their light decay time was only  $\approx .03 \mu\text{s}$  instead of  $.65 \mu\text{s}$ . The present work supports these findings and indicates that the deactivation of CsI(Na) is probably caused by the absorption of water from the air

## II. OBSERVATIONS

The responses of several CsI(Na) crystals to various radioactive sources which emit  $\alpha$ -particles and X-rays at different energies were measured. Each source was placed near the crystal which was optically coupled with Dow Corning silicon gel #20-057 to an RCA C31016F photomultiplier which has a bialkali photocathode and a peak response at  $4000\text{\AA}$ . The output from the photomultiplier was integrated with a time constant of  $0.4 \mu\text{s}$  and fed through a 256-channel pulse-height analyzer (Nuclear Data 1100).

The resulting differential pulse-height spectrum was displayed on an oscilloscope and in hard copy.

Using this experimental set-up the measurements of Crannell, et. al. [3] were repeated with several CsI(Na) crystals whose surfaces had been exposed for varying lengths of time to different atmospheric conditions. The differential pulse-height spectrum for the 4.8 MeV  $\alpha$ -particles emitted by  $\text{Am}^{241}$  incident on a fresh surface of CsI(Na) shows a high amplitude response sharply peaked ( $\text{FWHM} \approx 26\%$ ) at an equivalent X-ray energy of  $\approx 3$  MeV. The energy scale was calibrated with the crystal's response spectrum to the 1.170 MeV and 1.330 MeV X-rays emitted by  $\text{Co}^{60}$ . This agrees with the spectrum published by Menefee, et. al. [4] but their crystals had better resolution ( $\text{FWHM} \approx 8\%$ ).

Upon being exposed to the normal laboratory atmosphere, the response spectra of CsI(Na) crystals to  $\alpha$ -particles gradually decreases in amplitude, becomes broader and peaks at a lower equivalent X-ray energy. Eventually the peak can not be resolved from the noise. The range of an  $\alpha$ -particle in CsI is  $\approx 25 \mu$ , so this lack of a peak indicates a non-scintillating layer at least that thick. Crystals with smaller finite dead layers will display diminished response peaks. The two extrema and two intermediate cases are illustrated in Figure 1. The  $\text{Am}^{241}$  source used was not at all collimated, which was a factor in broadening the observed peaks. The response spectrum to a  $0.5 \mu\text{Ci } \text{Co}^{60}$  source is included in each case for reference.

Since  $\alpha$ -particles only penetrate  $25 \mu$  of CsI(Na), X-rays must be used to measure dead layers thicker than that. The probability,  $P$ , of an X-ray of energy,  $E$ , reaching a depth,  $D$ , in the crystal before being absorbed is:

$$P = \exp [-(\mu/\rho)_E \rho D]$$

where  $\rho$  is the density of CsI(Na) ( $4.51 \text{ g-cm}^{-3}$ ) and  $(\mu/\rho)_E$  is its mass attenuation coefficient in  $\text{cm}^2\text{-g}^{-1}$  at the energy  $E$ . The values of  $(\mu/\rho)_E$  for CsI(Na) were calculated from the elemental tables of Storm and Israel [5] and are plotted in Figure 2. If an X-ray is absorbed in the dead layer, the normal scintillation light will not be produced. Since the mass attenuation coefficient varies with energy, the relative response of a crystal to X-rays of two different energies can be used to determine the thickness of the dead layer.

$\text{Cd}^{109}$  was chosen to measure dead layers because this single source emits X-rays at two distinct energies, 22.162 keV and 87.9 KeV, in a known ratio of  $25.6 \pm 0.2$  to 1 for the 22  $\mu\text{Ci}$  source used. This ratio was measured with a 3" x 3" cylindrical NaI(Tl) crystal. For this specific source;

$$D = -128 \ln \left( \frac{N_X^{22}/N_X^{88}}{25.6} \right) \mu$$

where  $D$  is the thickness of the dead layer in microns and  $N_X^E$  is the total number of recorded pulses in response to incident X-rays of energy,  $E$  (in keV). Statistical errors of 6% in determining  $N_X^{22}/N_X^{88}$  give an accuracy of  $\pm 7 \mu$  in the calculated values of  $D$ .

The variation with energy in the probability that an X-ray will penetrate a dead layer is plotted in Figure 3 for the cases  $D = 1, 10, 100,$  and  $1000 \mu$ . It can be seen that even very thin dead layers cause severe attenuation of low energy X-rays.



### III. TEMPORAL DEVELOPMENT OF THE DEAD LAYER

Measurements were made over a period of  $\approx 5$  months of the dead layers on several CsI(Na) crystals. The results are displayed in Figure 4. Table 1 lists the method by which each crystal surface was exposed and the environment in which it was kept. With the exception of crystal F, all samples were originally part of the same crystal.

The rate of growth of the dead layer is closely related to the ambient humidity. Figure 4 shows the thickness of the dead layer on each surface plotted against the length of time it had been exposed. The anomalously high points at surface ages of one to three days are the true measured dead layers on the crystals which were placed in saturated atmospheres. They can be seen to represent comparable dead layers to those on the other crystals after a few months. Another crystal, which had been surrounded with desiccants and wrapped in plastic for over five years had a similar dead layer ( $264 \pm 11\mu$ ). The dead layer on the principle scintillator in the high-energy celestial X-ray detector on OSO-8 was found to increase from  $61 \pm 10\mu$  to only  $70 \pm 7\mu$  over a 57 day period shortly before launch during which it was kept in a room maintained at a dew point of  $\leq 5^{\circ}\text{C}$  and a temperature of  $\approx 20^{\circ}\text{C}$ . This supports my statement that a dead layer will grow more slowly in a drier atmosphere. A sealed plastic bag does not provide sufficient protection from the atmosphere, as can be seen from the similar growth rate of dead layers on crystals B and E. From the data it is impossible to determine if the dead layer stops growing after a certain point, but that is highly unlikely.

The fact that the dead layers on the polished surfaces of Crystal B grew more slowly than the others indicates that polishing a crystal can inhibit the deterioration of the surface. As corroborating evidence, the surfaces of the central crystals orbitted on OSO-5 and OSO-8 and the back-up crystals for OSO-8, which were all highly polished, had  $236 \pm 9 \mu$  dead layer after  $\approx 2400$  days,  $70 \pm 7 \mu$  dead layer after  $\approx 620$  days, and  $260 \pm 140 \mu$  dead layer after  $\approx 510$  days respectively. They were all exposed to a normal laboratory atmosphere except for the last few months prior to launch for the flight units during which time the ambient humidity was regulated to  $\approx 40\%$ . Keszthelyi-Lándori and Hrehuss[6] found that their CsI(Na) crystals had much better resolution when polished, but did not comment on the variation of the crystals' scintillation properties with time.

The destruction of the scintillation properties of a CsI(Na) crystal is not reversible by placing it in a vacuum to draw out the absorbed water. After spending two days in a saturated atmosphere crystal A was placed in a vacuum at a pressure of  $10^{-4}$  torr. After a total of 38 hours, the dead layers on the two polished surfaces of Crystal A were not significantly smaller than they had been before entering the vacuum ( $340 \pm 18 \mu$  on average as opposed to a previous average of  $410 \pm 35 \mu$ ).

#### IV. PHYSICAL PROPERTIES OF THE DEAD LAYER

When a severely damaged CsI(Na) crystal is illuminated by ultra-violet radiation, the dead layer can be easily distinguished from the

rest of the crystal. CsI(Na) fluoresces a brilliant indigo, whereas the response of a dead crystal to the same source is a pale yellow. The crystal is very transparent to both colors, so good and dead regions can be visually separated.

On badly damaged CsI(Na) crystals the deactivated layer can be literally peeled off or knocked off from the remaining good crystal. The resulting surface is piecewise very smooth, yet varies in height by up to a few millimeters. The now separate non-scintillating crystal is soft, slightly pliable, and easily divided into smaller pieces. The good crystal is very hard and difficult to break.

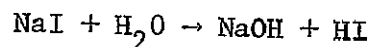
Although at any given position the edge of the dead layer is well defined, there is large variation in its thickness over small distances. The two back-up central crystals for the OSO-8 high-energy celestial X-ray detector were found to have an average dead layer of  $256\ \mu$  with  $\sigma = 56\%$ . The top and bottom side of each crystal were each measured in sixteen positions, evenly spaced across the  $50\ \text{cm}^2$  surface. An attempt was made to remove these dead layers by sanding. It was found that the decrease in thickness of dead layer was an average of 40% of the amount removed. When the initial average dead layer was thicker than  $100\ \mu$ , this figure was 72%. After removing an average of  $500\ \mu$  ( $\sigma=140\ \mu$ ) from each side of each crystal, the remaining dead layer had an average thickness of  $36\ \mu$  and an average standard deviation of the thickness on a given surface of 81%, or  $29\ \mu$ . Portions of this crystal were physically softer than others and got sanded down farther even though uniform pressure was ensured by wrapping the sandpaper around a wood block.

## V. DISCUSSION

Sodium ions in the crystal lattice of CsI create imperfections in the lattice structure. In CsI, as in many other crystals, these deviations result in a fluorescence which differs from and obscures that of the pure crystal by allowing transitions which are normally forbidden [7,8].

The specific impurity is critical to the nature of the resulting scintillation, as can be seen from the different characteristics of CsI(Na) and thallium activated cesium-iodide [CsI(Tl)], which have broad emission peaks at 4200Å and 5650Å respectively. For incident X-rays with energies between 22 keV and 835 keV, the light output from CsI(Na) was 2.72 times as great as that from CsI(Tl). The fluorescent responses of the crystals were determined by comparing various combinations of crystals and photomultipliers. [9] Tidd, et. al, [10] cite further differences between CsI(Na) and CsI(Tl).

With the absorption of water into a CsI(Na) crystal, the effect of the imperfections caused by the sodium in the lattice structure is eliminated. The process by which this happens is not known exactly, but there are indications that small sections of the crystal actually dissolve in the absorbed water and the reaction



occurs. After the Na has been removed from the lattice the remaining unactivated CsI recrystallizes. Although in solution the above reaction goes very fast in the opposite direction, a mass spectrograph revealed HI in a deactivated CsI(Na) crystal which implies that within the crystal this is not the case.

With a mass spectragraph it is impossible to determine the relative amount of HI and H<sub>2</sub>O in the crystal because HI vaporizes at a lower temperature and is driven off first. This destroys the equilibrium and more HI is formed to reattain it. The process of mass spectrometry itself forces a deceptively large amount of HI to be detected. It was useful in identifying the presence of HI in a CsI(Na) in small concentrations (of order 20 μg HI per 1g CsI) even though the technique cannot be used to determine absolute abundances. No non-destructive techniques were available for locating HI in such small quantities.

In the melt, that reaction goes as it would in solution. Brinckman[11] was able to produce CsI(Na) by adding NaOH, NaF, NaBr or NaI to a "CsI ultra-pure" melt. When he used NaOH he must have formed H<sub>2</sub>O as a by-product which had to be removed from the melt. He did not comment on the deterioration with time of crystals made in this way, so there is no indication of the amount of water left in the melt or of its later effect on the crystal.

Schrader [12] of the Harshaw Chemical Company, from whom my crystals were bought, would not reveal the method by which they entered Na into the melt, except to say that they used a salt. However, it is safe to say that within the crystal structure the Na exists as NaI which, even in the small concentrations in which it exists (≈ 50 μg NaI per 1g CsI), is sufficiently hygroscopic to transfer that property to the CsI(Na) crystal as a whole.

The facility with which dead portions of CsI(Na) crystals are broken, their softness and their pliability are all consistent with the theory that the crystal actually dissolves in the water it absorbs and recrystallizes into CsI crystallites, with the Na being taken out as NaOH. This is supported by the fact that the sodium concentration in a good part of crystal A was measured to be  $45.5 \pm 1.1 \mu\text{g/g}$ , whereas that in a dead region was only  $28.6 \pm 0.8 \mu\text{g/g}$ .

## VI. CONCLUSIONS

A deactivated layer on a CsI(Na) crystal seriously inhibits that crystal's scintillation response to X-rays, especially at lower energies. This non-uniform attenuation can be utilized to measure the thickness of the dead layer using a single  $\text{Cd}^{109}$  source, which emits X-rays at two distinct energies. Dead layers less than  $\approx 25 \mu$  thick can be measured with the crystal's response to  $\alpha$ -particles emitted by  $\text{Am}^{241}$ . If the thickness of the dead layer on a CsI(Na) detector is known, its effect must be included in the calculated detector efficiency. Source spectra determined using crystals with unaccounted for dead layers will be too weak at lower energies and the inferred spectral index will be too low.

CsI(Na) crystals which are intended for use as X-ray detectors should be polished and kept in as dry an environment as possible. The deteriorating effect of atmospheric water is not reversible by placing the crystal in a vacuum, so it should not be assumed that dead layers on crystals in satellite instruments will decrease or disappear after launch. Since even a very thin dead layer strongly attenuates X-rays below  $\approx 20 \text{ keV}$ , CsI(Na) detectors should not be used at these energies unless extreme precautions are taken to ensure that no dead layer forms on the crystals.

## VII. ACKNOWLEDGMENTS

It is a pleasure to thank Drs. Brian R. Dennis, Larry E. Orwig and Carol J. Crannell for their advice and assistance throughout the preparation of this paper.

### VIII. REFERENCES

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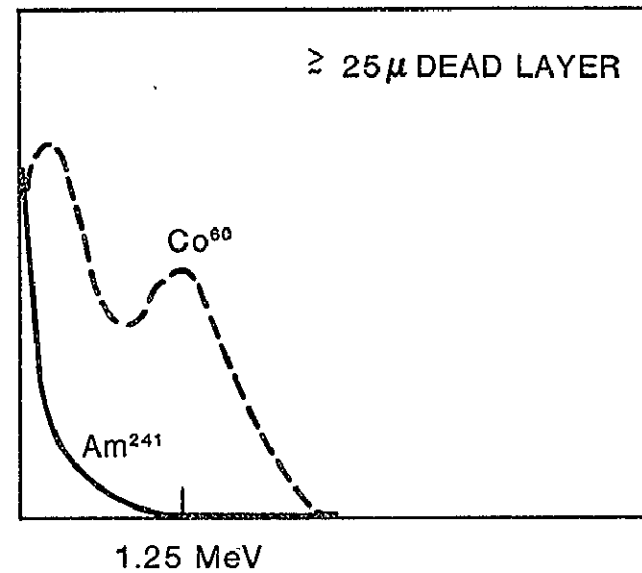
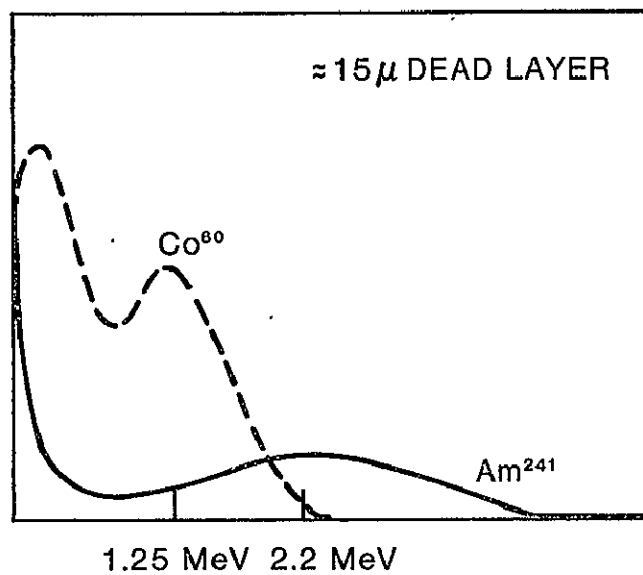
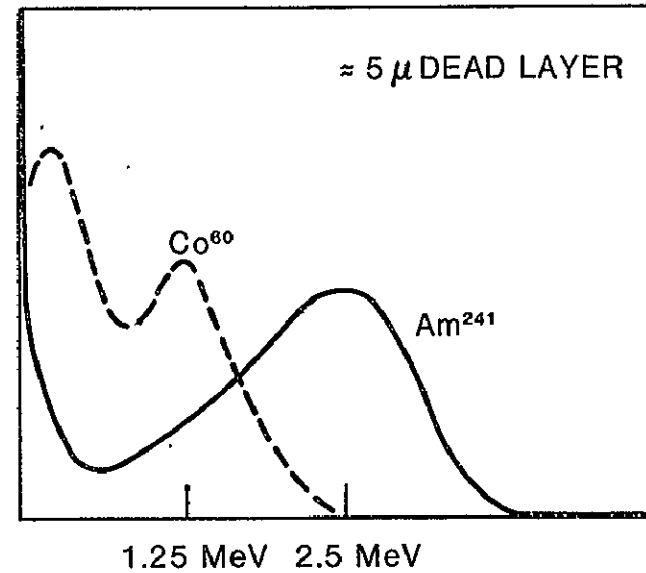
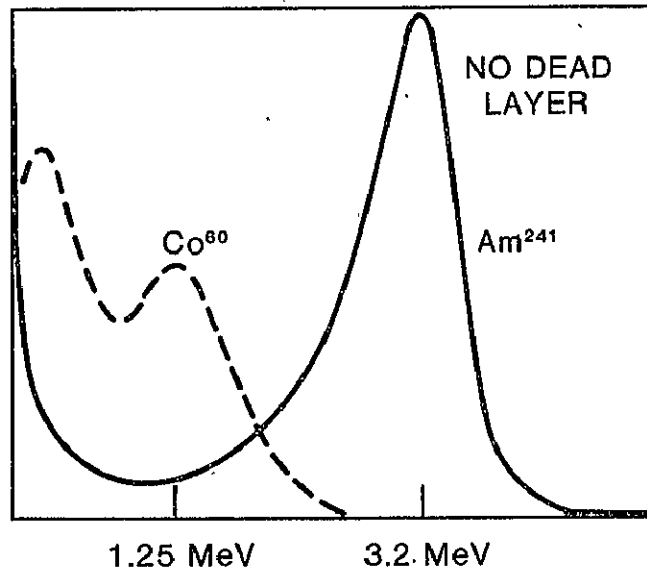


## IX. FIGURE CAPTIONS

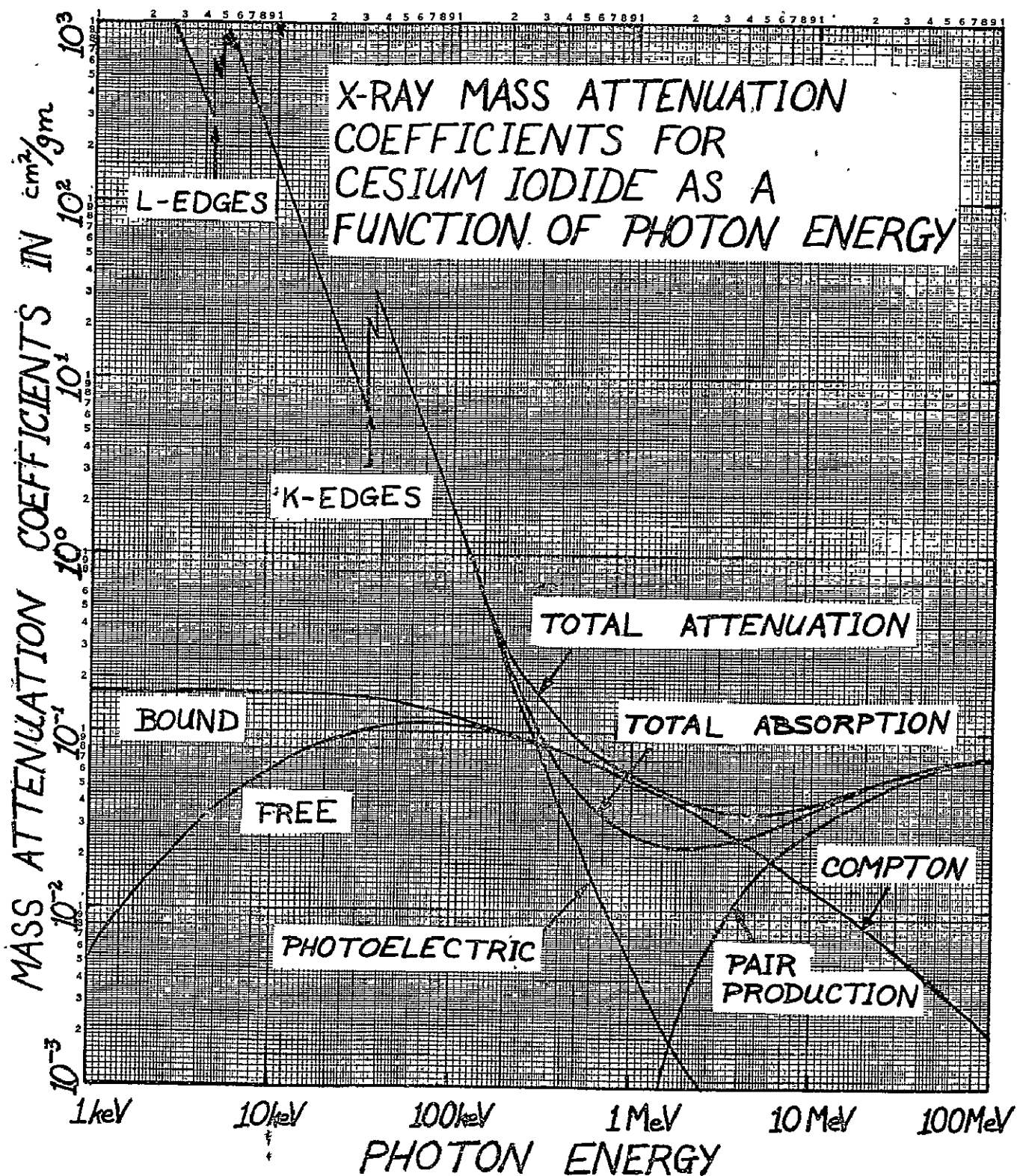
- Figure 1. Typical response spectra of CsI(Na) crystals with varying thicknesses of dead layers to the 4.8 MeV  $\alpha$ -particle emitted by  $\text{Am}^{241}$  (solid curve) and to the 1.170 MeV and 1.330 MeV X-rays emitted by  $\text{Co}^{60}$  (broken curves), which was used to calibrate the energy scale. The thickness of the dead layer for each of four cases illustrated is indicated. The spectra were obtained with a 256-channel pulse height analyzer using a RCA C31016F photomultiplier with a bialkali response.
- Figure 2. The X-ray mass attenuation coefficients for CsI plotted as a function of photon energy. These curves were computed from the tables given by Storm and Israel [5] using a CsI composition of 51.15% Cs and 48.85% I by weight. In CsI(Na), the Na is only  $\approx .004\%$  by weight and makes no noticeable changes to the mass attenuation coefficients.
- Figure 3. The probability of transmission of an incident X-ray through a dead layer of 1, 10, 100 and 1000 $\mu$  on a CsI(Na) crystal as a function of photon energy. These curves were derived from the mass attenuation coefficients for CsI plotted in Figure 2.
- Figure 4. The dead layers on several CsI(Na) crystals as a function of the age of each surface. The method by which each surface was exposed and the conditions in which it was kept are listed in Table 1.

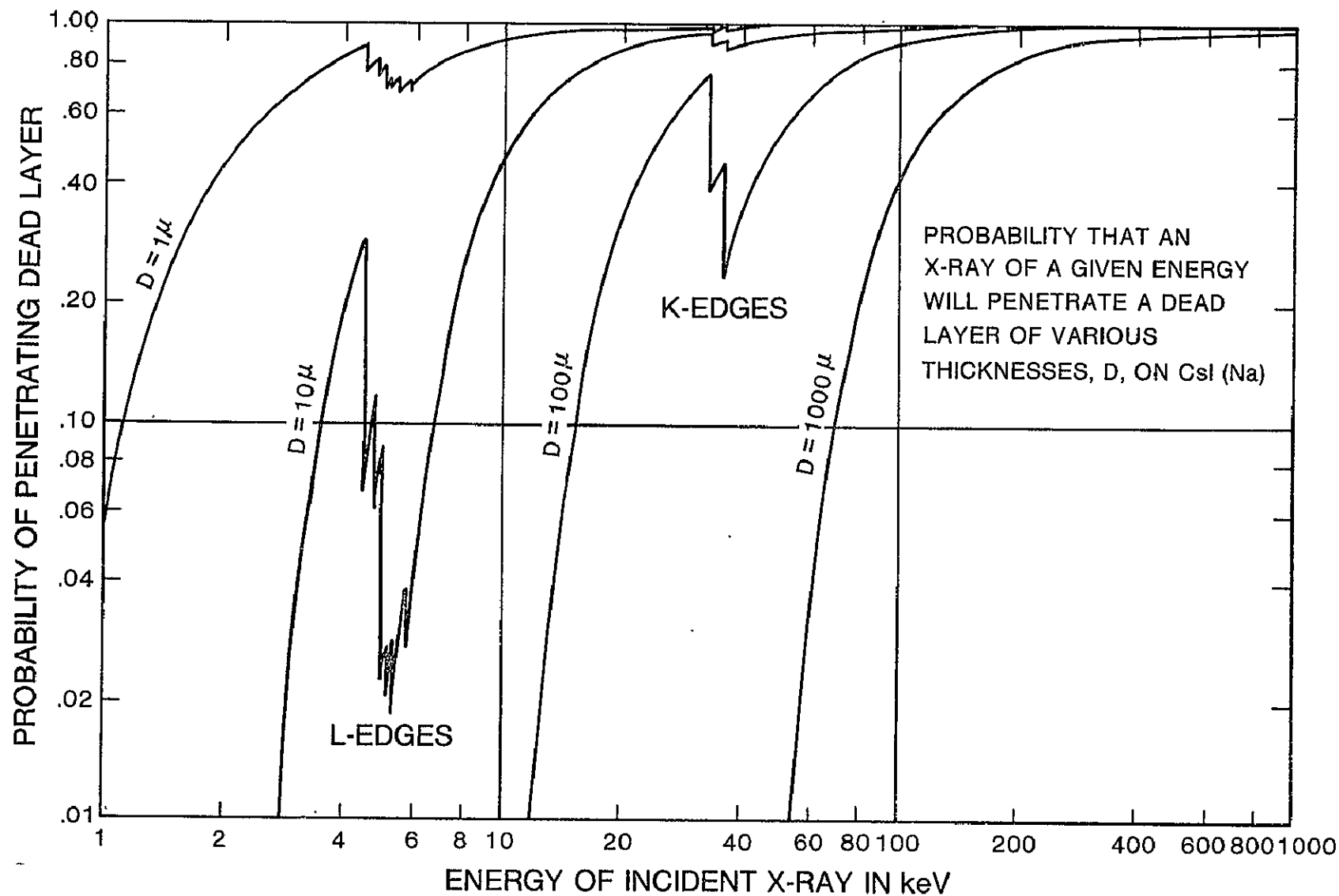
(★ : Crystal A, sides 1, 2; ☆: Crystal A, side 3;  
■: Crystal B, sides 1, 2; □: Crystal B, side 3;  
▲ : Crystal C; △ Crystal D; ○: Crystal E,  
● : Crystal F)

RESPONSE SPECTRA OF CsI (Na) TO  $\text{Co}^{60}$  AND  $\text{Am}^{241}$  WITH VARYING THICKNESSES OF DEAD LAYERS



# X-RAY MASS ATTENUATION COEFFICIENTS FOR CESIUM IODIDE AS A FUNCTION OF PHOTON ENERGY





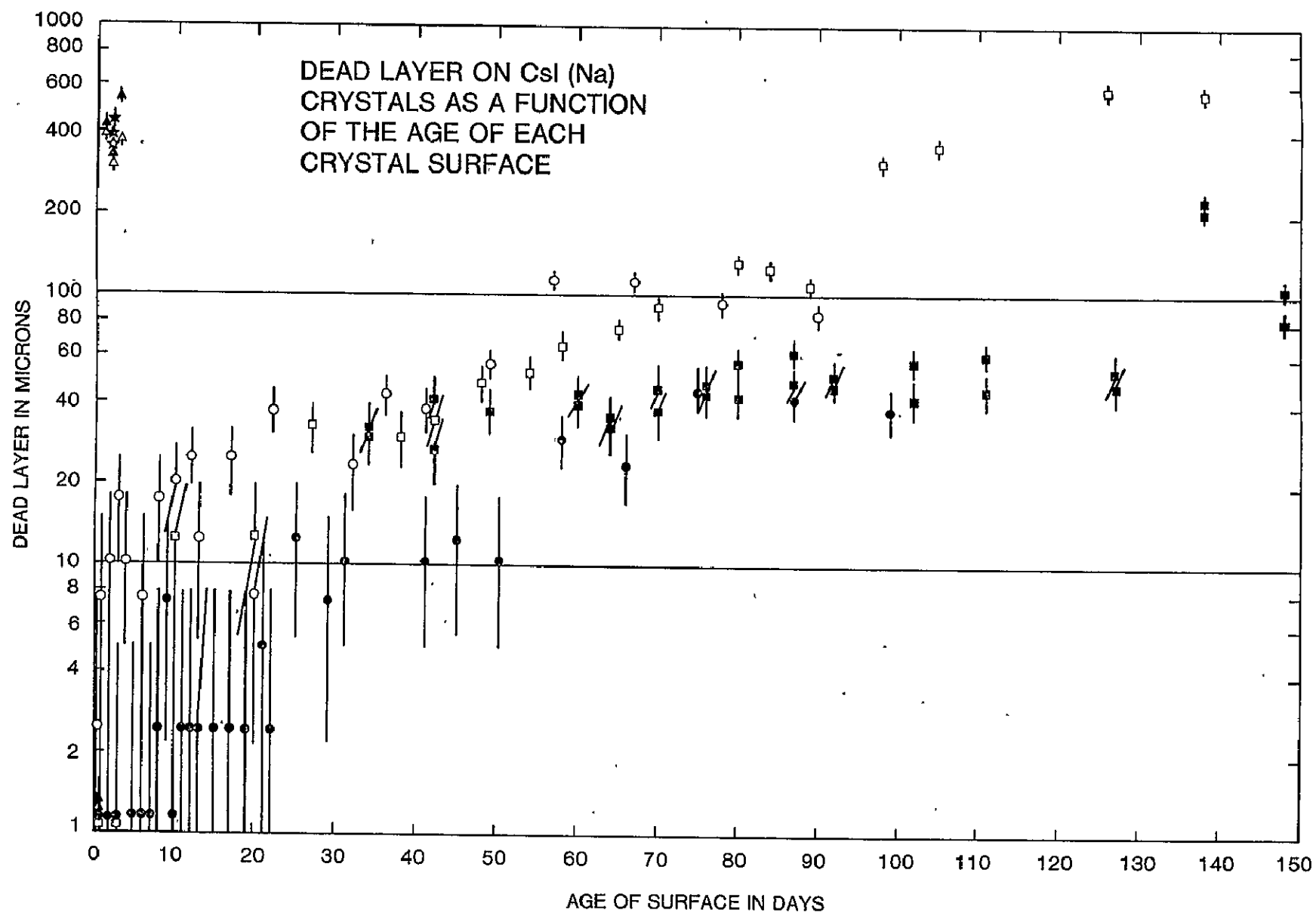


TABLE 1: METHOD OF EXPOSING CRYSTAL'S SURFACES AND CONDITIONS IN WHICH THEY WERE KEPT

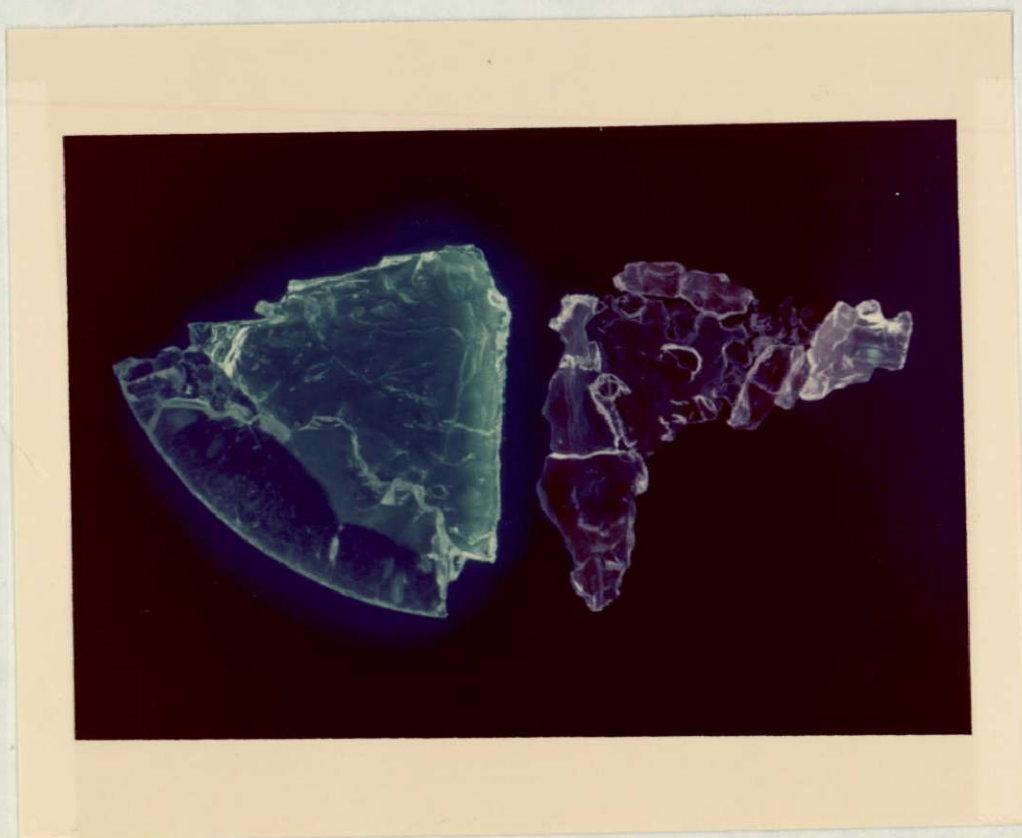
CRYSTAL NAME	SYMBOL IN FIGURE 4	HOW SURFACE WAS EXPOSED	CONDITION IN WHICH CRYSTAL WAS KEPT
A - Sides 1, 2	★	Surface sanded and polished	} Open to 100% Relative humidity
A - Side 3	☆	Crystal broken with hammer and chisel	
B - Sides 1, 2	■	Surface sanded and polished	} Kept in sealed zip-lock plastic bag
B - Side 3	□	Crystal broken with hammer and chisel	
C	▲	Crystal broken with hammer and chisel	Open to 100% relative humidity
D	△	Crystal broken with hammer and chisel	Open to 100% relative humidity
E	○	Dead layer peeled off	Kept in unsealed paper envelope
F	●	Dead layer peeled off	Kept in sealed zip-lock envelope
OSO-5 Flight Central Crystal	—	Surface machined and polished	Open to room atmosphere
OSO-8 Flight Central Crystal	—	Surface machined and polished	Open to room atmosphere then kept at 40% relative humidity
OSO-8 Back-up Central Crystals	—	Surface machined and polished	Open to room atmosphere

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#### APPENDIX

A CsI(Na) crystal with a portion of it which has been peeled off and which no longer scintillates. The two pieces of the same crystal were illuminated by short-wave ultraviolet radiation and can be seen to have quite disparate fluorescent responses. Unfortunately, due to the properties of the photographic paper it was impossible to obtain exact duplication of the colors. Although the colors are slightly inaccurate, the difference between the two crystals is clear. The variation in thickness of the dead layer is also apparent.



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